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(54) Plastic sheet, a process for the manufacture thereof and formed articles containing the sheet

Kunststoffolie, Verfahren zu ihrer Herstellung und Formkörper, die die Folie enthalten

Feuille en matière plastique, procédé de fabrication de cette feuille, et articles contenant cette feuille

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04.05.1994 Bulletin 1994/18(73) Proprietor: AXXIS N.V.
B-8700 Tielt (BE)(72) Inventor: Venema, Gertjan
B-8740 Pittem (BE)(74) Representative:
Bleukx, Lucas Lodewijk Maria, Ir.
OCTROOIBUREAU DSM
Postbus 9
6160 MA Geleen (NL)(56) References cited:

EP-A- 0 368 637	EP-A- 0 411 136
US-A- 4 041 206	US-A- 4 859 726
US-A- 4 983 653	US-A- 4 983 711

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Description

The invention relates to a plastic sheet containing a copolymer, which copolymer is obtainable by reacting dimethyl terephthalate or terephthalic acid with a mixture of 99-55 mole % ethylene glycol and 1-45 mole % cyclohexane dimethanol.

Such a sheet is known from US-A-4.355.080.

An advantage of such a sheet is that the use of the copolymer imparts to the sheet high toughness and, if the sheet is of a transparent type, a high degree of transparency, which high toughness and high transparency are wholly or almost wholly retained when the plastic sheet is formed into an end product at elevated temperature.

A disadvantage, however, is that the copolymer exhibits poor weatherability. The sheet, on exposure to weather conditions, becomes less transparent, yellow and brittle, so that the sheet is not suited for use in outdoor applications such as glazing for buildings and greenhouses, noise barriers, advertising boards and guards.

DE-A-2.853.631 shows that it is not possible to improve the weatherability of such a copolymer with a relatively low cyclohexane dimethanol content by adding a UV light-absorbing additive.

The United States patent mentioned above therefore proposes to laminate the sheet with an acrylic film so as to improve the weatherability, the acrylic film optionally containing a UV light-absorbing additive.

A disadvantage hereof is that bonding problems may arise between the acrylic film and the sheet, rendering the sheet unfit for use.

The invention aims to provide a sheet that does not have the disadvantage referred to above.

Surprisingly, this is accomplished as a result of there being present at least one surface of the sheet a 2 to 100- μm layer also containing the copolymer and a UV light-absorbing additive.

The sheet according to the invention exhibits good weatherability without the disadvantage of the bonding problems of the known sheet.

It is true that EP-A-320632 describes a plastic sheet to which is applied a layer containing a plastic and a UV light-absorbing additive, but the plastic is different from the copolymer contained in the sheet according to the invention and no indication is to be found in it as to how the surprisingly good result of the sheet according to the invention is to be obtained.

A further advantage of the sheet according to the invention is that such a sheet can be formed into end products in a simple manner at elevated temperature, whilst with the known sheet this is made difficult by the presence of the acrylic film.

Yet another advantage is that the sheet according to the invention can readily be recycled whilst the known sheet is very difficult to recycle, if at all, inasmuch as the sheet contains two different plastics.

The term sheet as used in this application means a body whose thickness is only small in relation to its length and width. The term sheet should be taken to include film, foil, and so forth as well. The term sheet should also be taken to include twin wall sheet. The sheet may be flat or curved. By sheet surfaces is meant the two outer faces of the sheet that are perpendicular to the direction of the thickness.

The copolymer contained in the sheet is preferably obtainable by reacting dimethyl terephthalate or terephthalic acid with a mixture of 98-60 mole % ethylene glycol and 2-40 mole % cyclohexane dimethanol. The copolymer contained in the sheet is more preferably obtainable by reacting dimethyl terephthalate or terephthalic acid with a mixture of 97-66 mole % ethylene glycol and 3-34 mole % 1,4-cyclohexane dimethanol.

Such a sheet possesses good mechanical properties and, if it is of a transparent type, a high degree of luminous transmittance.

The copolymer contained in the sheet is more preferably obtainable by reacting dimethyl terephthalate or terephthalic acid with a mixture of 95-70 mole % ethylene glycol and 5-30 mole % cyclohexane dimethanol.

In principle, any UV light-absorbing additive suited for use in thermoplastic polyesters or copolymers may be employed in the sheet according to the invention, such as those mentioned in DE-A-2853631, EP-A-247480, EP-A-320632 and Plastics Additives Handbook, 3rd edition, Hanser Publishers, of Munich, (1990) page 176 and following pages.

A benzotriazole or a benzophenone is preferably employed as UV light-absorbing additive.

2-Hydroxyphenyl benzotriazoles with the general formula 1 as given in the sheet of formulas, for instance, may be used.

In these formulas:

- R¹ is an alkyl group containing 1-18 C atoms or an aryl alkyl group containing 18 C atoms.
- R² is a hydrogen atom or a chlorine atom or an alkyl group containing 1-18 C atoms or an aryl alkyl group containing 7-18 C atoms.

Examples of benzophenones that are suited for use in the sheet according to the invention are represented by the general formula 2 as shown on the sheet of formulas. Here, R is a hydrogen atom or an alkyl group containing 1-12 C atoms.

Preferably, a benzotriazole whose molecules contain 2 benzotriazole groups is used in the sheet according to the invention, for instance a benzotriazole group with the general formula 3 in the sheet of formulas.
Here:

- 5 R¹ and R², which may be either the same or different, are a hydrogen atom or a halogen atom, an alkyl group containing 1-10 C atoms, a cycloalkyl group containing 5-10 C atoms, an aryl alkyl group containing 7-13 C atoms, an aryl group
 10 containing 6-14 C atoms, -OR⁷ or COOR⁷. R⁷ is a hydrogen atom or an alkyl group containing 1-10 C atoms, a cycloalkyl group containing 5-10 C atoms, an aryl alkyl group containing 7-13 C atoms or an aryl group containing 6-14 C atoms.
- R³ and R⁴, which may be either the same or different, are a hydrogen atom, an alkyl group containing 1-15 C atoms, a cycloalkyl group containing 5 or 6 C atoms, an aryl alkyl group containing 7-20 C atoms or an aryl group containing 6-14 C atoms.
 - R⁵ and R⁶, which may be either the same or different, are an alkyl group containing 2-15 C atoms, a cycloalkyl group containing 5-10 C atoms, an aryl alkyl group containing 7-20 C atoms, an aryl group containing 6-14 C atoms, -OR⁷ or -COOR⁷.
 - a and b, which may be the same or different, are 1, 2, 3 or 4.
 - c and d, which may be the same or different, are 1, 2 or 3.

- The benzotriazoles whose molecules contain 2 benzotriazole groups have a high molecular weight and, hence, evaporate or migrate less rapidly from the plastic sheet than the UV light-absorbing additives which have a lower molecular weight.
- 25 The layer containing the copolymer and the UV light-absorbing additive may be present at only one surface of the sheet. In that case, however, only the surface where the layer containing the copolymer and the UV light-absorbing additive is present should be exposed to the weather.
 It is preferred for the layer containing the copolymer and the UV light-absorbing additive to be present at both surfaces of the plastic sheet.
- 30 The layer containing the copolymer and the UV light-absorbing additive generally contains 0.5-20% by wt. of UV light-absorbing additive. The layer preferably contains 1-15, and more preferably 2-10% by wt. of UV light-absorbing additive.
 The plastic sheet is produced by any one of the processes known in plastics technology. For instance, the sheet may be produced by extruding or calendering a sheet containing the copolymer and pressing onto the sheet, just before it cools down, a 2-100-μm film containing the copolymer and the UV light-absorbing additive. It is also possible to apply 35 to the sheet a layer of a solution containing the copolymer and the UV light-absorbing additive and then allow the solvent to evaporate.
 The plastic sheet is preferably produced by coextruding in a single step the layer or the layers containing the copolymer and the UV light-absorbing additive and the remaining part of the sheet. Such a plastic sheet exhibits good optical properties and there exists a good bond between the layers and the remaining part of the sheet.
- 40 Preferably the thickness of the layer is 3-50 μm, more preferably 5-40 μm.
 The plastic sheet may contain the usual additives such as lubricants, antioxidants, optically active additives and colorants. In addition, if it is of a non-transparent type, the plastic sheet may contain, for instance, pigments, fillers and fibres.
 The plastic sheet may be processed into shaped articles for instance by forming the plastic sheet at elevated temperature, by bending or folding at ambient temperature and, optionally, machining, for instance cutting and sawing.
- 45 The invention also relates to shaped articles wholly or partially produced from the sheet according to the invention, such as riot shields, visors, covers, skylights, glazing in greenhouses, noise barriers and buildings, and advertising boards.

Examples 1, 2 and comparative example A, B, C

- 50 Compounds were prepared by melting ethylene-1,4 cyclohexylene dimethylene terephthalate (Kodar PETG® 6763, supplied by Eastman of the USA) in the usual manner in a twin-screw kneader and mixing it with a UV light-absorbing additive.
 The compositions of the compounds were as follows:
- compound 1: 93% by wt. PETG 6763, 7% by wt. 2-(2H-benzotriazole-2-yl)-4,6-bis-(1-methyl-1-phenyl ethyl)phenol (Tinuvin® 234, supplied by Ciba Geigy of Switzerland).
 - compound 2: 95% by wt. PETG 6763, 5% by wt. bis(2-hydroxy-5-t-octyl-3-(benzotriazole-2-yl)phenyl)-methane (Mixxim® BB/100, supplied by Claus Huth GmbH of Germany).

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Plastic sheets 4 mm thick and 1250 mm wide were coextruded, comprising a core layer of substantially the nominal thickness and at either surface a surface layer of about 40 µm.

The core layer consisted of 100 % PETG 6763. Both surface layers of plastic sheet 1 consisted of compound 1 whilst both surface layers of plastic sheet 2 consisted of compound 2. In addition plastic sheets A, B and C were extruded without the surface layers. The thickness of sheet A was 4 mm and the sheet consisted solely of PETG 6763. The thickness of sheet B was 0.75 mm and the sheet consisted at 0.3% by wt. bis(2-hydroxy-5-t-octyl-3-(benzotriazol-2-yl)phenyl)-methane and 99.7% PETG 6763.

The thickness of sheet C was 4 mm and the sheet consisted of 0.02% by weight bis-(2-hydroxy-5-t-octyl-3-(benzotriazol-2-yl)phenyl)-methane and 99.98 PETG 6763. The plastic sheets 1, 2 and A were subjected to the following tests:

- 10 1) Accelerated weathering in a QUV Accelerated Weathering tester (R), supplied by The Q-Panel Company of the USA, equipped with QUV-B313 lamps. The exposure times were 500 and 1000 hours. The weathering cycle was comprised of 4 hours' UV irradiation at 60°C alternated with 4 hours' condensation at 50°C. Before and after weathering, the yellowness index (YI) was measured according to ASTM D 1925, the luminous transmittance (LT) and the impact resistance by the falling weight impact measurement according to ASTM D 3029.
- 15 2) Accelerated weathering in a Xenon Weather-Ometer® supplied by Atlas of the USA. The radiation intensity was 0.35 W/m² at a wavelength of 340 nm. Borosilicate/borosilicate filters were installed. The blackpanel temperature was 63°C. The weathering cycle comprised 102 minutes' dry exposure alternated with 18 minutes' wet exposure. The exposure times were 1000, 2000 and 3000 hours. The YI and the LT were measured before and after weathering.
- 20 3) Natural weathering by placing the plastic sheets out in the open in accordance with DIN 53386 at Tielt (Belgium). The YI and the LT were measured before and after weathering.

The results for plastic sheets 1 and 2 according to the invention and plastic sheet A without the surface layers are given in Tables 1-3.

TABLE 1

Results before and after weathering in QUV Accelerated Weathering Tester			
Plastic sheet	Hours exposed		
	0 hours	500 hours	1000 hours
YI (-)			
A	3.5	9.0	12.0
1	5.1	4.7	5.8
2	5.2	5.7	5.4
LT (%)			
A	84	82	79
1	84	82	82
2	84	83	83
MLE (J)			
A	45	5	-
1	45	41	-
2	45	41	-

The YI, LT and MLE of the plastic sheets according to the invention appear to be hardly affected, if at all, by the weathering treatment, in contrast with the plastic sheet without the surface layer, which strongly yellows, becomes less transparent and embrittles rapidly.

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The YI of the sheets according to the invention is admittedly at a somewhat higher level, but the value remains constant during use of the sheets. This latter aspect is determining for the applicability of the sheets.

TABLE 2

Results before and after weathering in Xenon Weather-Ometer				
Plastic sheet	Hours exposed			
	0 hrs	1000 hrs	2000 hrs	3000 hrs
YI(-)				
A	3.5	10.3	12.3	14.0
1	5.1	3.9	4.2	5.1
2	5.2	4.3	4.6	4.8
LT(%)				
A	84	82	80	78
1	84	84	84	83
2	84	84	84	84

The YI and the LT of the plastic sheets according to the invention appear to be hardly affected, if at all, by the weathering treatment, in contrast with the plastic sheet without the surface layer, which strongly yellows and becomes less transparent. Furthermore, after weathering for a brief period, the plastic sheet without the surface layer developed a pronounced haze whilst this was hardly the case, if at all, with the plastic sheets according to the invention.

TABLE 3

Results before and after natural weathering		
Plastic sheet	Time exposed	
	0 year	0.5 year
YI (-)		
A	3.0	9.6
1	4.5	4.0
2	5.0	4.2
LT(%)		
A	84	83
1	84	84
2	84	84
MLE (J)		
A	45	6
2	45	42

The YI-LT and the MLE of the plastic sheets according to the invention appear to be hardly affected, if at all, by the weathering treatment, in contrast with the plastic sheet without the surface layer, which strongly yellows, becomes less transparent and becomes brittle.

The plastic sheets B and C were subjected to the test in the QUV Accelerated Weathering Tester.

TABLE 4

Results before and after weathering in the QUV Accelerated Weathering Tester			
Plastic sheet	Hours exposed		
	0 hrs	500 hrs	1000 hrs
YI (-)			
B	11.9	13.9	14.2
C	11.6	-	-
LT (%)			
B	87.5	84.8	84.1
C	81.7	-	-

From these results, it can be seen that, even the initial YI of both sheet B and C being as bad as the YI of the 1000h QUV-weathered sheet A (table 1). The sheets B and C are commercially valueless.

The QUV-Accelerated Weathering results for sheet B further show that, upon 500 h and 1000 h exposure, the YI increases further and to a much higher extend than the sheets according to the invention, comprising the surface layer.

Claims

1. Plastic sheet containing a copolymer, which copolymer is obtainable by reacting dimethyl terephthalate or terephthalic acid with a mixture of 99-55 mole % ethylene glycol and 1-45 mole % 1,4-cyclohexane dimethanol, characterized in that at least one surface of the sheet a layer with a thickness of 2 to 100 µm is present, which layer also contains the copolymer and a UV light-absorbing additive.
2. Plastic sheet according to claim 1, characterized in that the copolymer is obtainable by reacting dimethyl terephthalate or terephthalic acid with a mixture of 98-60 mole % ethylene glycol and 2-40 mole % 1,4-cyclohexane dimethanol.
3. Plastic sheet according to claim 1, characterized in that the copolymer is obtainable by reacting dimethyl terephthalate or terephthalic acid with a mixture of 97-66 mole % ethylene glycol and 3-34 mole % 1,4-cyclohexane dimethanol.
4. Plastic sheet according to claim 1, characterized in that the copolymer is obtainable by reacting dimethyl terephthalate or terephthalic acid with a mixture of 95-70 mole % ethylene glycol and 5-30 mole % 1,4-cyclohexane dimethanol.
5. Plastic sheet according to any one of claims 1-4, characterized in that a benzotriazole or a benzophenone is used as UV light-absorbing additive.
6. Plastic sheet according to claim 5, characterized in that the benzotriazole contains two benzotriazole groups in each molecule.
7. Plastic sheet according to any one of claims 1-6, characterized in that the layer containing the copolymer and the UV light-absorbing additive is present at both surfaces.
8. Plastic sheet according to any one of claims 1-7, characterized in that the layer containing the copolymer and the UV light-absorbing additive contains 1-15% by wt. of the UV light-absorbing additive.
9. Process for the production of a sheet according to any one of claims 1-8, characterized in that the layer containing the copolymer and the UV light-absorbing additive is applied by means of a coextrusion process.

10. Shaped articles wholly or partially produced from the sheet according to any one of claims 1-9.

Patentansprüche

- 5 1. Kunststoffbahn enthaltend ein Copolymer, welches Copolymer durch Umsetzung von Dimethylterephthalat oder Terephthalsäure mit einer Mischung von 99-55 Mol-% Ethylenglykol und 1-45 Mol-% 1,4-Cyclohexandimethanol erhältlich ist, dadurch gekennzeichnet, daß an zumindest einer Oberfläche der Bahn eine Schicht mit einer Dicke von 2 bis 100 µm vorhanden ist, welche Schicht auch das Copolymer und einen UV-Licht-absorbierenden Zusatz enthält.
 - 10 2. Kunststoffbahn nach Anspruch 1, dadurch gekennzeichnet, daß das Copolymer durch Umsetzung von Dimethylterephthalat oder Terephthalsäure mit einer Mischung von 98-60 Mol-% Ethylenglykol und 2-40 Mol-% 1,4-Cyclohexandimethanol erhältlich ist.
 - 15 3. Kunststoffbahn nach Anspruch 1, dadurch gekennzeichnet, daß das Copolymer durch Umsetzung von Dimethylterephthalat oder Terephthalsäure mit einer Mischung von 97-66 Mol-% Ethylenglykol und 3-34 Mol-% 1,4-Cyclohexandimethanol erhältlich ist.
 - 20 4. Kunststoffbahn nach Anspruch 1, dadurch gekennzeichnet, daß das Copolymer durch Umsetzung von Dimethylterephthalat oder Terephthalsäure mit einer Mischung von 95-70 Mol-% Ethylenglykol und 5-30 Mol-% 1,4-Cyclohexandimethanol erhältlich ist.
 - 25 5. Kunststoffbahn nach einem der Ansprüche 1-4, dadurch gekennzeichnet, daß ein Benzotriazol oder ein Benzophephon als UV-Licht-absorbierender Zusatz verwendet wird.
 - 30 6. Kunststoffbahn nach Anspruch 5, dadurch gekennzeichnet, daß das Benzotriazol zwei Benzotriazolgruppen in jedem Molekül enthält.
 7. Kunststoffbahn nach einem der Ansprüche 1-6, dadurch gekennzeichnet, daß die Schicht enthaltend das Copolymer und den UV-Licht-absorbierenden Zusatz an beiden Oberflächen vorhanden ist.
 - 35 8. Kunststoffbahn nach einem der Ansprüche 1-7, dadurch gekennzeichnet, daß die Schicht enthaltend das Copolymer und den UV-Licht-absorbierenden Zusatz 1-15 Gew.-% des UV-Licht-absorbierenden Zusatzes enthält.
 9. Verfahren zur Herstellung einer Bahn nach einem der Ansprüche 1-8, dadurch gekennzeichnet, daß die Schicht enthaltend das Copolymer und den UV-Licht-absorbierenden Zusatz mittels eines Coextrusionsverfahrens aufgebracht wird.
10. Formgegenstände, die ganz oder teilweise aus der Bahn nach einem der Ansprüche 1-9 hergestellt worden sind.

Revendications

1. Feuille en matière plastique contenant un copolymère, lequel copolymère peut être obtenu en faisant réagir du téréphthalate de diméthyle ou de l'acide téréphthalique avec un mélange de 99-55 moles % d'éthylène glycol et de 1-45 moles % de 1,4-cyclohexane diméthanol, caractérisée en ce que, sur au moins une surface de la feuille, une couche d'une épaisseur de 2 à 100 µm est présente, laquelle couche contient aussi le copolymère et un additif absorbant l'ultraviolet.
2. Feuille en matière plastique selon la revendication 1, caractérisée en ce que le copolymère peut être obtenu en faisant réagir du téréphthalate de diméthyle ou de l'acide téréphthalique avec un mélange de 98-60 moles % d'éthylène glycol et de 2-40 moles % de 1,4-cyclohexane diméthanol.
3. Feuille en matière plastique selon la revendication 1, caractérisée en ce que le copolymère peut être obtenu en faisant réagir du téréphthalate de diméthyle ou de l'acide téréphthalique avec un mélange de 97-66 moles % d'éthylène glycol et de 3-34 moles % de 1,4-cyclohexane diméthanol.
4. Feuille en matière plastique selon la revendication 1, caractérisée en ce que le copolymère peut être obtenu en faisant réagir du téréphthalate de diméthyle ou de l'acide téréphthalique avec un mélange de 95-70 moles % d'éthylène

glycol et de 5-30 moles % de 1,4-cyclohexane diméthanol.

5. Feuille en matière plastique selon l'une quelconque des revendications 1-4, caractérisée en ce qu'on utilise un benzotriazole ou une benzophénone comme additif absorbant l'ultraviolet.
6. Feuille en matière plastique selon la revendication 5, caractérisée en ce que le benzotriazole contient deux groupes benzotriazole dans chaque molécule.
7. Feuille en matière plastique selon l'une quelconque des revendications 1-6, caractérisée en ce que la couche contenant le copolymère et l'additif absorbant l'ultraviolet est présente sur les deux surfaces.
10. Feuille en matière plastique selon l'une quelconque des revendications 1-7, caractérisée en ce que la couche contenant le copolymère et l'additif absorbant l'ultraviolet contient 1-15 % en poids de l'additif absorbant l'ultraviolet.
15. 9. Procédé pour la production d'une feuille selon l'une quelconque des revendications 1-8, caractérisé en ce que la couche contenant le copolymère et l'additif absorbant l'ultraviolet est appliquée au moyen d'une co-extrusion.
10. Articles produits entièrement ou partiellement à partir de la feuille selon l'une quelconque des revendications 1-9.

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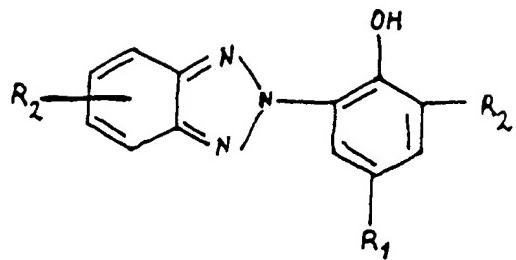
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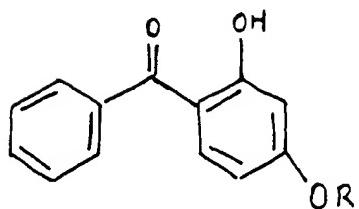
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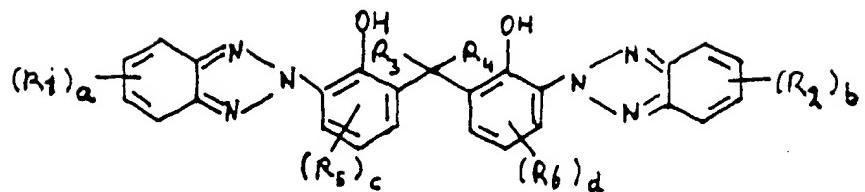
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Formula 1



Formula 2



Formula 3